

RECOVERING NICKEL

The present invention relates to a process for recovering valuable metals, such as nickel, from liquors obtained by processing laterite ores and concentrates of the ores that are contaminated with high levels of iron.

The term "processing laterite ores and concentrates" is understood herein to include processing by any one or more of heap leaching, pressure leaching, bacterial oxidation leaching, and atmospheric tank leaching.

The present invention relates particularly, although by no means exclusively, to a process for recovering nickel and cobalt from liquors obtained by acid leaching ores and concentrates of the ores that are contaminated with high levels of iron.

In this context, the term "high levels of iron" is understood to mean levels of iron whereby the mole ratio of Fe:Ni is greater than 2:1.

It is known that nickel can be recovered from such liquors containing nickel by contacting the liquors with H_2S to precipitate nickel sulphides (and mixed sulphides in situations where nickel and other valuable metals such as cobalt are in the liquors).

However, it is also known that iron will co-precipitate as a sulphide under conventional H_2S precipitation conditions and that such co-precipitation is undesirable from the viewpoint of optimising recovery of nickel (and cobalt).

It is known that iron can be removed from liquors prior to nickel (and cobalt) precipitation by using (a)

- 2 -

high temperatures (180-220°C) to selectively precipitate iron as hematite (b) low temperatures (90-120°C) to precipitate iron as goethite, and low temperatures (70-150°C) to precipitate iron as jarosite. However, high
5 temperature precipitation is capital intensive, requiring autoclaves and flash vessels, and low temperature precipitation results in high nickel losses as a result of nickel adsorption onto iron species.

10 The applicant has developed a process that is capable of recovering very high levels (greater than 99%) of nickel from nickel liquors with very low levels of co-precipitation of iron.

15 According to the present invention there is provided a process for recovering valuable metals from laterite ores and concentrates that are contaminated with iron, which process includes the steps of:

20 (a) reducing ferric ions to ferrous ions in a leach liquor containing a valuable metal and iron in solution using a suitable reductant, the leach liquor being obtained by processing laterite ores or concentrates of the ores that contain the
25 valuable metal and are contaminated with iron ;

(b) neutralising the liquor to reduce the free acid concentration in solution to levels suitable for nickel precipitation; and

30 (c) precipitating the valuable metal using the reductant and seed particles under process conditions, including one or more of seed particle size, seed composition, and
35 temperature, that are selected to maximise nickel precipitation and to minimise iron precipitation.

- 3 -

Preferably the reduction step (a) includes reducing ferric ions to ferrous ions using the reductant in the presence of 40-90 g/l free acid.

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The reductant may be any suitable reductant.

One suitable reductant is NaHS.

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Preferably the reductant is a gaseous reductant.

Preferably the gaseous reductant is H_2S .

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Preferably the neutralisation step (b) increases the pH of the solution to 2.

Preferably the neutralisation step (b) maintains iron in the ferrous state.

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Preferably the valuable metal is nickel.

More preferably the valuable metals are nickel and cobalt.

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Preferably the laterite ores are ores that contain nickel in a chlorite mineral phase.

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Preferably the process conditions for the precipitation step (c) include operating at a partial pressure of the gaseous reductant of less than 60 psi.

More preferably the gas partial pressure is less than 40 psi.

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More preferably the gas partial pressure is less than 30 psi.

- 4 -

It is preferred particularly that the gas partial pressure be less than 25 psi.

5 Preferably the process conditions for the precipitation step (c) include operating at a liquor temperature of at least 50°C.

10 More preferably the liquor temperature is at least 60°C.

15 Preferably the seed particles for the precipitation step (c) have a particle size of P_{50} less than 100 micron.

20 More preferably the particle size of the seed particles is P_{50} less than 80 micron.

25 It is preferred particularly that the particle size of the seed particles be P_{50} less than 60 micron.

30 Preferably the seed particle concentration for the precipitation step (c) is greater than 30g/l.

35 More preferably the seed particle concentration is greater than 40g/l.

40 Preferably the ratio of iron and the valuable metal in the leach liquor supplied to step (a) is greater than 2:1.

45 More preferably the ratio is greater than 3:1.

50 More preferably the ratio is greater than 5:1.

55 The present invention is based on extensive experimental work carried out by the applicant to recover nickel and cobalt from laterite ores. The experimental

- 5 -

work included the following work.

EXPERIMENTAL

5 Initial sulphide precipitation test work using a gaseous reductant in the form of H_2S gas in the presence of seed particles was carried out on synthetic liquor generated by dissolving technical grade sulphate salts in tap water.

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The initial test work included test work for optimal precipitation conditions using the synthetic liquor.

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The initial test work investigated the following precipitation parameters to determine their effect on nickel and cobalt recovery and nickel/iron separation:

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- Temperature
- H_2S pressure
- Seed particle size
- Seed concentration,

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The initial test work for optimal precipitation conditions was conducted under the following conditions:

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- Agitation = 750 rpm with twin axial turbines
- Sampling time = 15, 30 and 60 minutes (in some instances a 120 minute sample was also taken).
- Seed chemistry = synthetic NiS , $Ni:S = 0.95$

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Once the optimal conditions for sulphide precipitation were determined, further tests were conducted using liquors generated from heap leaching of laterite ores from a range of different sources. The different sources are referred to as GA-Ev, GA-Tr, GL-Ka, and GL-Ak in the following description.

- 6 -

The heap leach liquors were spiked with nickel and cobalt sulphate salts to increase the nickel and cobalt concentration in solution to ~4 and 0.2 g/l respectively to simulate recycling of liquor to the heap.

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Analysis of the liquors used in the test work is given in Table 1.

Table 1 - Liquor Compositions

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Liq. Source	^D Ni	Co	^D Fe	^D Mg	Cr	^D Al	Mn	Cu	Zn	^D FA
Synthetic	4.04	198	24.9	5.94	526	8.00	706	1	5	1.0
GA-Ev	4.16	204	26.0	4.58	593	4.46	470	5	5	80
GA-Tr	4.02	196	22.6	3.62	749	3.91	511	4	3	86
GA-Ka	4.20	200	16.4	13.4	108	0.272	313	3	73	45
GA-Ak	4.25	210	27.2	4.82	518	4.88	455	3	3	73

Assays are in mg/L

D denotes assays in g/L

Sulphide product assays were all back calculated to discount the seed component.

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RESULTS

Effect of Temperature on Mixed Sulphide Precipitation

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Temperature influences the precipitation process through its influence on H₂S solubility and the dissociation equilibrium constant for H₂S.

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The kinetics of precipitation are also influenced by temperature.

The effect of temperature on metal precipitation was determined under the following conditions:

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Seed P ₅₀	-	109 microns
H ₂ S pressure	-	30 psi
Seed concentration	-	30 g/L
Residence Time	-	60 minutes

- 7 -

The detailed results for Tests 1 to 4 from these tests are summarised in Figure 1.

5 The results show that increasing the temperature increased metal precipitation. Metal precipitation increased dramatically between 40°C and 60°C and there was only a marginal increase in metal precipitation between 80°C and 95°C after 60 minutes. The Ni:Fe mole ratio
10 ranged from 7 to 10 between 60 and 95°C and appears to reach a maximum at 80°C and then decrease again at 95°C.

 Precipitation of aluminium, magnesium, manganese and chromium were low (<1%) under the conditions
15 investigated.

Effect of Seed Charge

 In commercial operations seed particles are added
20 to facilitate precipitation. It is expected that as the seed surface area increases the kinetics of precipitation increases, thereby resulting in a lower S^{2-} concentration in solution, and enabling better selectivity for nickel and cobalt over iron.

25 The surface area of seed particles can be increased by increasing the mass of seed in the reactor or by seeding with solids with a smaller average particle size. The influence of both factors was investigated.
30 Detailed results are summarised in Figures 2 and 3.

 The results show that nickel and cobalt recovery increased with the mass of seed added and with a decreasing average seed particle size. Both these
35 observations are consistent with nickel and cobalt recovery increasing with increasing seed surface area.

- 8 -

When the seed particle size was reduced from $P_{50} = 109$ microns to $P_{50} = 45$ microns nickel recovery increased from 98.2 to 99.5% while cobalt recovery increased from 99.0 to 99.7%.

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Using the finer seed had little effect on the Ni:Fe mole ratio in the product which appeared to decrease slightly from 7.0 to 6.7. This change in the Ni:Fe ratio is probably not significant within the errors of the experiment.

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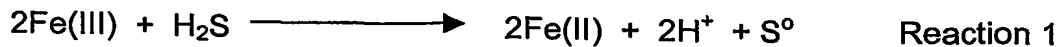
When the seed concentration was increased from 30 to 50g/l a similar increase in nickel and cobalt recoveries was observed. However, significantly, the Ni:Fe mole ratio in the product decreased from 7.0 to 4.7 due to iron precipitation increasing from 2.2 to 3.2%. These results are inconsistent with those observed with the finer seed. A possible explanation is that the test using the higher seed concentration (Test 10) was conducted significantly later than all the other tests and oxidation of the ferrous ions in the feed liquor appears to have resulted in a higher ferric ion concentration in this solution relative to the previous tests. This is supported by the higher free acid concentration in solution at the end of Test 10 (~17g/l as opposed to ~8g/l previously) and the higher sulphur concentration (62% S as opposed to 48% S) in the sulphide product. Both these observations are consistent with H_2S reacting with Fe(III) in solution according to the following reaction.

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The above reaction produces free acid and elemental sulphur as observed in test 10. The presence of Fe(III) in solution would also be expected to have

- 9 -

resulted in higher iron precipitation, reducing the Ni:Fe mole ration in the sulphide product.

Effect of Hydrogen Sulphide Pressure

Previous test work indicated that H₂S pressure between 30 and 60 psi had a strong influence on metal precipitation. In the current test work the effect of H₂S pressure was investigated further.

Precipitation tests were conducted at 80°C, 30 g/l seed, with a P₅₀ of 109 microns. The results are presented in Figure 4.

The results show that nickel recovery increased from 97.1 to 99.8% while cobalt recovery increased from 96.8 to 99.7% as H₂S pressure increased from 20 to 40 psi while the Ni:Fe mole ratio of the product decreased from 11.3 to 6.6. This corresponds to iron precipitation increasing from 1.3 to 2.3%.

These results are all consistent with S²⁻ concentration in solution increasing with H₂S partial pressure resulting in greater metal recovery and lower selectivity.

Column Heap Leach Liquors

From the above series of tests the following optimal conditions required for precipitating nickel and cobalt from heap leach liquors were determined:

- H₂S Pressure 20 psi
- Seed charge 30 g/l
- Temperature 80°C
- Seed P₅₀ 45 microns.

- 10 -

Initially, heap leach liquors were partially neutralised to remove excess free acid and then treated with H₂S to precipitate nickel and cobalt without a pre-reduction stage. This resulted in low nickel and cobalt precipitation and the product was contaminated with iron and elemental sulphur. In addition, the liquor free acid also increased sharply, according to reaction 1.

A second batch of liquors was generated and treated in the following sequence of process stages, as discussed below:

- Pre-reduction
- Neutralisation
- Sulphide Precipitation

Pre-Reduction Stage

The following pre-reduction stage was selected with the objective of reducing all Fe(III) to Fe(II):

Temperature 80°C
H₂S pressure 20 psi
Reaction time 90 minutes
Initial free acid 40-90 g/l H₂SO₄

The results are summarised in Table 2.

Table 2 - Results of Pre-Reduction with H₂S

Sample	% Precipitation				Final Aq. Assays (g/L)			
	Ni	Co	Cu	Zn	Cr	Fe(II)	Fe	F.A
GL-Ev	0.25	0.01	94	0.24	0.02	26.7	26.7	101
GL-Tr	0.67	0.01	87	0.46	0.02	22.2	22.1	104
GL-Kaa	0.08	0.01	81	0.01	0.003	16.7	17.3	58.2
GL-Ak	0.13	0.005	76	0.30	0.12	26.4	26.6	95

The Fe(III) was effectively reduced to Fe(II)

- 11 -

under the conditions employed.

Nickel and cobalt precipitation were minimal. Nickel precipitation ranged from 0.083 to 0.67% while
5 cobalt precipitation was less than 0.01%.

Copper was the only element which showed significant precipitation, with copper concentrations in solution reduced to less than 1 mg/l.

10 The concentrations of the other elements assayed (Fe, Zn, Cr, Mg, Mn and Al) were not significantly altered by the pre-reduction stage with precipitation consistently being less than 0.5% and typically less than 0.1%.

15 As a result of the Fe(III) reduction the free acid concentration increased and elemental sulphur was generated.

20 The observed increase in free acid concentration in solution was in good agreement with the calculated increase in free acid concentration based on reaction 1 stoichiometry.

25 Residue assays showed sulphur as the main constituent (>80%).

30 The results show that the Fe(III) could be effectively reduced to Fe(II) using H₂S in the presence of relatively high free acid (40-90 g/l) with minimal nickel and cobalt losses. This is a positive outcome.

Neutralisation Stage

35 The liquors generated from the pre-reduction stage were treated with limestone to increase the solution pH to ~2 in the neutralisation stage.

The feed liquor compositions supplied to the neutralisation stage are given in Table 3.

5 Table 3 - Liquor Compositions to Neutralisation Stage

Liq. Source	^D Ni	Co	^D Fe	^D Mg	Cr	^D Al	Mn	Cu	Zn	^D FA
GL-Ev	4.27	210	26.7	4.80	622	5.12	497	0.4	5	101
GL-Tr	4.07	197	22.1	3.83	758	4.32	519	0.5	3	104
GL-Ka	4.43	197	17.3	14.2	119	0.347	330	0.6	77	58
GL-Ak	4.14	196	26.6	4.94	565	5.45	470	0.7	3	95

Assays are in mg/L

D denotes assays in g/L

10 The liquors were neutralised by being treated with limestone ($P_{80}=250$ microns) at ambient temperature. The results of the neutralisation tests are summarised in Table 4.

15 Table 4 - Results of Liquor Neutralisation

Sample	% Precipitation				Final Aq. Assays (g/L)			
	Ni	Co	Fe	Zn	Cr	Fe(II)	Fe	pH
GL-Ev	0.37	0.07	0.11	3	0.1	26.8	27.9	2
GL-Tr	0.40	0.16	0.01	14	1	22.0	22.5	2
GL-Ka	0.26	0.05	0.17	0.2	4	15.6	17.3	2
GL-Ak	0.33	0.15	0.10	9	2	26.1	28.3	2

Nickel and cobalt losses by precipitation were low - ranging from 0.2 to 0.4% and 0.05% to 0.16%,
 20 respectively.

The copper concentration in solution was reduced to below the copper detection limit of 0.1 mg/l.

25 Precipitation of the remaining impurities (Al, Mn, Cr, Fe and Zn) was low, generally less than 1%.

The iron essentially remained in the Fe(II) state enabling sulphide precipitation from the liquor to be
 30 undertaken.

- 13 -

The residues were mainly composed of gypsum (indicated by high calcium and sulphur assays).

5 Limestone consumption was very high, ranging from 13 to 24 kg/kg (Ni + Co) - due to the high free acid concentration in the solution.

10 Overall nickel and cobalt losses across pre-reduction and neutralisation stages were low, ranging from 0.3 to 1.1% and 0.06 to 0.17%, respectively.

Sulphide Precipitation Stage

15 Following the pre-reduction and neutralisation stages the clarified liquors were treated with H₂S to precipitate nickel and cobalt under the following conditions.

- 20
- H₂S Pressure 20 psi
 - Seed charge 30 g/l
 - Temperature 80°C
 - Seed P₅₀ 45 microns.

25 The composition of the liquors used in the sulphide precipitation stage are summarised in Table 5.

Table 5 - Liquor Compositions to
Sulphide Precipitation Stage

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Sample	Liquor Assay (mg/L)								
	Ni	Co	Fe	Cu	Cr	Al	Mn	Zn	Mg
GL-Ev	4250	210	27940	0.2	621	5080	497	5	4780
GL-Tr	4050	197	22510	0.2	750	4260	519	3	3810
GL-Ka	4420	197	17280	0.2	114	347	330	77	14220
GL-Ak	4130	196	28340	0.4	554	5410	470	3	4930

The results of sulphide precipitation are summarised in Table 6.

Table 6 - Results of Sulphide Precipitation

Liquor	% Precipitation			Solids Assays (%)							Solids #Ni:Fe
	Ni	Co	Fe	Ni	Co	Fe	Cr	Al	Zn	S	
GL-Ev	99.2	99.0	1.7	47.6	2.3	5.0	0.13	0.05	0.03	30.8	9.0
GL-Tr	99.3	99.8	1.9	47.5	2.5	4.3	0.08	0.03	0.01	29.7	10.6
GL-Ka	99.3	99.6	2.7	48.7	2.3	4.6	0.02	0.01	0.73	31.3	10.1
GL-Ak	99.4	99.8	1.3	47.0	2.4	4.0	0.10	0.04	<0.01	32.1	11.2

Mole Ratio

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Despite the relatively low H₂S partial pressure, nickel and cobalt recoveries were high (>99%).

10 In optimisation test work the same H₂S pressure and temperature yielded recoveries of ~97% for nickel and cobalt.

15 The higher recoveries observed with the heap leach solutions is attributed to using a finer seed P₅₀=45 microns compared to P₅₀=109 microns for the synthetic solutions. The sulphate levels were similar for synthetic and real liquors (~100 g/l SO₄²⁻) and were not expected to have resulted in significant differences in nickel and cobalt precipitation.

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The solids contained between 4.0 and 5.0% Fe with the Ni:Fe mole ratio ranging between 9.0 and 11.2.

25 These results are in good agreement with the results obtained under similar conditions in the optimisation test work.

30 The results showed that the Ni:Fe mole ratio could be upgraded from a range of 0.14-0.24 in solution to 9.0-11.2 in the sulphide product representing approximately a 50 fold upgrade of the nickel values with respect to iron.

- 15 -

Aluminium and chromium showed increased precipitation as the concentration of these metals in solution increased. However the concentrations of aluminium and chromium in the product remained low. These results are summarised in Figure 5.

The aluminium concentration in the product generally increased with aluminium concentration in solution. Aluminium does not form stable sulphides in solution and the increase in aluminium concentration in the product appears to be through adsorption/entrainment with the sulphide.

The chromium concentration in the product also increased with chromium concentration in solution. This effect is much stronger with the increase in chromium in the product increasing more steeply with chromium in the PLS compared to aluminium and could indicate that chromium precipitated as opposed to being adsorbed/entrained.

Zinc concentration in solution was reduced to between 2 and 3 mg/l. The sulphide products were generally low in zinc (less than 0.03%) due to the relatively low zinc concentration in solution (3-5 mg/l). Only the sulphide generated from the GL-Ka ore contained significant zinc at 0.73% due to the feed solution having a higher zinc tenor (77 mg/l).

Copper concentration in the products was low due to copper removal in previous unit operations with copper in the product ranging between 0.01 and 0.03%.

Manganese and magnesium concentrations in the products were consistently low at less than 50 ppm and less than 500 ppm, respectively, reflecting the high selectivity of sulphide precipitation against these

elements.

CONCLUSIONS

5 From the test work the following conclusions can
be drawn.

- 10 1. Nickel and cobalt precipitation increased as liquor
temperature increased from 40°C to 95°C. The Ni/Fe
separation appeared to reach a maximum at 80°C.
Aluminium, chromium, manganese and magnesium
precipitation were not affected over the temperature
range investigated.
- 15 2. Increased seed surface area increased nickel and
cobalt recovery.
- 20 3. Increasing the partial pressure of H₂S from 20 to 40
psi increased nickel recovery from 97.1 to 99.8% and
the cobalt recovery from 96.8 to 99.7%. The Ni:Fe
mole ratio in the product decreased from 11 to 6.7.

 From the test work conducted on the heap leach
liquors the following conclusions can be drawn.

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- 30 1. Liquors can be treated with H₂S gas in a pre-
reduction stage to reduce Fe(III) to Fe(II) with low
nickel and cobalt losses (ranging from 0.08% - 0.67%
and <0.1%, respectively). Copper was the only
impurity significantly removed during pre-reduction
with copper concentration in solution being reduced
below 1 mg/l.
- 35 2. The neutralisation stage effectively increased the pH
of the liquor from the pre-reduction stage to ~2
while maintaining iron in the Fe(II) state. Nickel
and cobalt losses during the neutralisation stage

- 17 -

were 0.2%-0.4% and 0.05%-0.16%, respectively. The residues were mainly gypsum. Impurity removal during neutralisation was generally less than 1%.

- 5 3. Sulphide precipitation was successful in precipitating greater than 99% of the nickel and cobalt, producing a precipitate with a Ni:Fe mole ratio between 9 and 11.2, from solutions containing ~
10 4g/L nickel and 17-27 g/l iron. Chromium and to a lesser extent aluminium were present in the sulphide product in minor quantities. Zinc concentration in solution was reduced to ~3 mg/l.

- 15 Many modifications may be made to the present invention described above without departing from the spirit and scope of the invention.